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LETTER TO THE EDITOR

Anomalous temperature dependence of the resistivity of some intermetallic compounds

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Abstract. The resistivity ρ of some intermetallic compounds such as Nb_3Sn, V_3Si, UAl_2, etc, has an anomaly at a temperature T_0 near 100 K. The resistivity rises steeply with T below T_0 and less steeply above it. Here we account for this anomalous temperature dependence using the 'classical' s–d model. Below T_0 the s-like and d-like states are hybridised by a small electronic matrix element J_{sd} ($J_{sd} \approx 10$–50 meV) and the electron–phonon coupling constant λ is large. Above T_0 the electron–phonon scattering rate $\hbar/\tau$ exceeds J_{sd}, and the s-like and d-like states are decoupled. The electrical conductivity is then due mainly to the s-like states which possess a smaller electron–phonon coupling constant λ, giving rise to a smaller value of $d\rho/dT$. The anomaly occurs when the mean free path l is about an order of magnitude larger than the interatomic spacing d.

Some time ago it was observed that many intermetallic compounds—particularly those which are high-temperature superconductors and are based either on the A15 (Nb_3Sn; Fisk and Webb 1976) or C15 (ZrV_2; Fisk and Lawson 1973) crystallographic phases—had an anomalous behaviour in the temperature dependence of their resistivities. Other similar materials, based on the same crystallographic phase but which are not high-temperature superconductors, did not show such anomalous behaviour. The classical cases of Nb_3Sn and Nb_3Sb were considered by Fisk and Webb (1976). Their data are shown in figure 1. At low temperatures both resistivities increase rapidly with temperature. The increase for Nb_3Sn is substantially faster than that for Nb_3Sb. At approximately 100 K the rapid increase of the Nb_3Sn resistivity shows a break and $d\rho/dT$ decreases; above ambient temperature it decreases further. The increase is linear from 400 to 800 K and $d\rho/dT$ is approximately 45 $\mu\Omega$ cm per 1000 K. For V_3Si the increase is approximately 55 $\mu\Omega$ cm per 1000 K up to 1200 K (Marchenko 1973). The 'knee' near 100 K is peculiar to A15 compounds which are high-temperature superconductors, and is not observed in low-temperature superconductors such as Nb_3Sb, for example. However, a similar behaviour has been observed in UAl_2 (Arko *et al* 1973), which is not a superconductor, and in the Chevrel phase $Pb_{0.9}Mo_{6.4}S_8$ under pressure (Nerz *et al* 1980).

It has been suggested (Allen 1980, Allen and Chakraborty 1981, Yu and Anderson 1984) that this behaviour may be associated with a very short mean free path l, the resistivity tending to saturate as $l \approx a$ where a is the lattice constant. However, from

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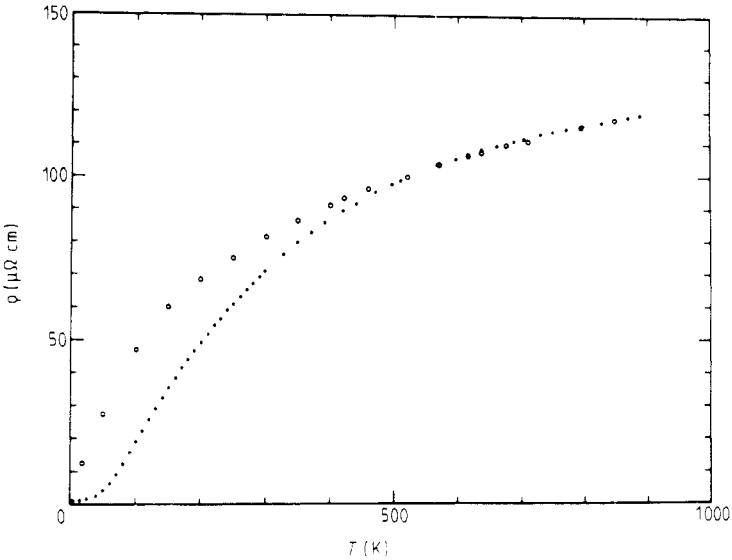

Figure 1. The resistivity of Nb_3Sn (○) and Nb_3Sb (●) as a function of temperature (Fisk and Webb 1976).

positron annihilation data on V_3Si we know the shape of the Fermi surface (FS) (Berko and Weger 1970, Samoilov *et al* 1981, Jarlborg *et al* 1983): it consists of several sheets, the largest one having six necks in the (100) direction and a volume of about 60–70% of the first Brillouin zone (BZ). There is a cube with a volume of about 10–15% of the BZ around Γ and some cylinders with smaller volumes along the line M–R. Thus the total volume of the FS is approximately 80–90% of the BZ, and there are about 1.6–1.8 carriers (electrons and holes) per unit cell. Thus the density of carriers n is approximately 1.5×10^{22} cm^{-3}. The value of k_F (defined to be in the first BZ) of the largest sheet is approximately $0.6\pi/a$ along the (111) direction, increasing to $1.0\pi/a$ towards the (100) direction. The average is about $0.8\pi/a$. This establishes a mean free path (where $\sigma = ne^2 l/\hbar k_F$) of about 25 Å at 100 K ($\rho \approx 50\,\mu\Omega$ cm) and about 10 Å at 800 K ($\rho \approx 125\,\mu\Omega$ cm); the values for Nb_3Sn and V_3Si are close. The lattice constant is $a = 4.72$ Å for V_3Si and $a = 5.30$ Å for Nb_3Sn. The interatomic spacing d is half this value. Thus $l \approx 10d$ at the temperature where the break occurs, and is still about $4d$ at the highest temperature measured. In Ti_3Sb, where the resistivity is about $400\,\mu\Omega$ cm at ambient temperature (Fisk and Webb 1976), it is indeed possible that $l \approx d$. In Nb_3Sn and V_3Si ρ continues to increase linearly with T up to the highest temperatures and there is no indication of saturation. Elastic scattering by radiation-damage centres, for example, behaves in a somewhat similar way (Gurvitch 1980, Muller *et al* 1980, Roulier-Albenque *et al* 1984).

Since the anomalous behaviour is also observed in UAl_2, it is not unique to high-temperature superconductors. However, all these intermetallic compounds possess sharp peaks in the density of states close to the Fermi level (Weger and Goldberg 1973, Weger 1978b, Van Kessel *et al* 1978, Mattheiss and Weber 1982, Mueller *et al* 1984); the half width of the peaks, as well as their separation from the Fermi level, is about 10–50 meV.

Should we expect a saturation of the resistivity?

Ioffe and Regel (1960) have suggested that the resistivity would saturate when the mean

free path becomes comparable with the interatomic distance, $l \approx d$. Such a saturation is indeed observed in some liquid metals and intermetallic valence metals where the resistance may be due to s–f scattering. This saturation is not a universal phenomenon: in Si:P at zero temperature, σ tends continuously to zero with decreasing P concentration. This is associated with the approach to Anderson localisation, which is normally linked to extensive broadening of the band due to disorder (which does not occur here). However, there is evidence (Mott and Kaveh 1983) that in Si:P the Anderson transition can occur in an unbroadened conduction band. Kaveh and Mott (1983) have suggested that this is possible only in a many-valley conduction band. In organic metals like TTF–TCNQ ρ shows no sign of saturation as $l \approx d$: rather, $d\rho/dT$ continues to increase (Cooper *et al* 1975); this is hopping conductivity, as manifested by a change of the susceptibility from a Pauli-like behaviour to a Curie one (Entin-Wohlman *et al* 1984).

In our case, however, we are still far from the Ioffe–Regel limit. At 100 K, $l \approx 10d$. Alternatively, we can consider the quantity $k_F l$, which suggests a change in behaviour when it becomes of order unity. In the present case, k_F is small ($\approx 0.8\pi/a$, $a = 2d$). However, when we consider the wavefunction in detail, we find that the main Fourier components occur at $\boldsymbol{p}_F = \boldsymbol{k}_F + \boldsymbol{G}$, where $\boldsymbol{G}$ is a reciprocal lattice vector. In the (100) direction, $G \approx 2\pi/a$. The small value of k_F indicates a very small modulation of the wavefunction with period $2\pi/k_F$. Positron annihilation data (Berko and Weger 1970, Samoilov *et al* 1981) indicate which Fourier components are strong. Along the (111) direction there are strong components in the Brillouin zones centred around points $(100)2\pi/a$ and $(110)2\pi/a$, but the components in the first zone are so weak that they cannot be observed. Thus, when we use a value of p_F in the extended zone of approximately $(\frac{1}{2} + 2)\pi/a$, the value of $p_F l$ is approximately 15π at the temperature at which the break in the ρ against T curve occurs, and about $(5–6)\pi$ at the highest temperature (800 K for Nb_3Sn, 1200 K for V_3Si); thus we are still very far from the temperature where the Ioffe–Regel rule may apply, or where non-classical diffusion (Anderson *et al* 1983) may be expected. Therefore the linear increase of ρ with T up to the highest temperatures is not surprising.

A key feature of this work is the low value that we use for n, the density of conduction electrons, and S, the area of the Fermi surface. This low value of n results in a large value for l of the 's' band. A conventional way to determine S is from the electronic specific heat γ^* and the critical field dH_{c_2}/dT (Orlando *et al* 1979). This method is appropriate for a *single* band. In the present case, when we have two bands differing widely in the values of m^*, v_F and l, the value of l determined by this method will be dominated by the 'd' band, since γ^* and dH_{c_2}/dT are almost unaffected by the 's' band. Thus this method is not appropriate for determining l of the 's' band, and therefore we use the value of S determined by actual measurements of the FS and band-structure calculations.

For some time the resistivity of transition metals has been described by the s–d model (Mott and Jones 1936), in which scattering between s and d states plays the dominant role. Let us consider here a modification of this classical theory, adapted to materials with a fine structure in the electronic density of states.

Consider two bands, denoted by 's' and 'd', that intersect close to the Fermi level (figure 2(*a*)) and a matrix element J_{sd} connecting the two bands. By 's' band we really mean the broad bands—the idea being that these could in fact contain components of s-, p-, or even d-state symmetries. The important point is that the 's' band has a large value of v_F, characteristic of free electrons. The 'd' band has a substantially smaller value of v_F, and hence makes a large contribution to the density of states. J_{sd} is only one component of the s–d interaction, that responsible for the small splitting of the two energy levels.

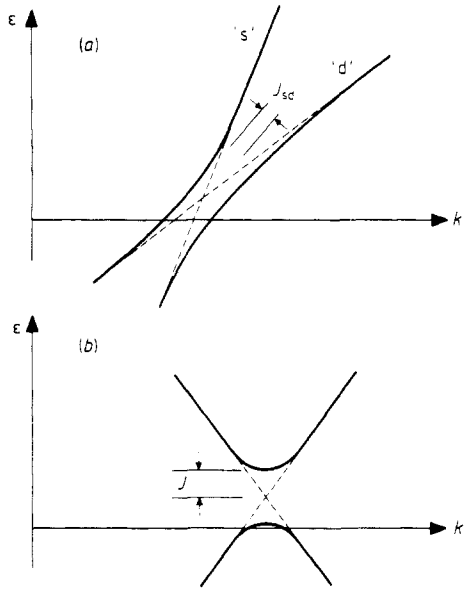

Figure 2. (*a*) Two energy levels, one with a large value of v_F ('s') and one with a small value ('d'), nearly cross near E_F and are connected by a matrix element J_{sd}. At low T the states are hybridised. At higher temperature the hybridisation is broken by the electron–phonon coupling. (*b*) Two levels with a comparable value of v_F cross. Here a sharp peak in the density of states at E_F is caused by the hybridisation. This peak disappears at higher temperatures when the hybridisation is broken by the electron–phonon coupling.

The eigenstate is given by

$$\psi = \alpha\psi_s + \beta\psi_d$$

where $|\alpha|^2 + |\beta|^2 = 1$. Normally, scattering by phonons (and other scatterers) takes place between these eigenstates. However, when J_{sd} is very small we encounter a new situation. Assume that the scattering, at time $t = 0$, is into state s. Thus

$$\psi = \psi_s$$

at $t = 0$. At time t

$$\psi(t) = \psi_s \cos(J_{sd}\, t/\hbar) + \psi_d \sin(J_{sd}\, t/\hbar)$$

(assuming for simplicity that $\alpha = \beta = 1/\sqrt{2}$). Another scattering takes place at time τ. Then the probability to be in an 's' state is given by $\cos^2(J_{sd}\,\tau/\hbar)$ and the probability to be in a 'd' state is given by $\sin^2(J_{sd}\,\tau/\hbar)$. When $J_{sd}\,\tau/\hbar \ll 1$, the effect of the matrix element J_{sd} to cause hybridisation is suppressed. τ can be estimated from the Hopfield (1970) relation $\hbar/\tau = 2\pi\lambda k_B T$. For $\lambda \approx 1.2$–1.5, $\hbar/\tau$ approaches 100 meV already at 100 K; thus, for $J_{sd} \approx 10$–50 meV, the hybridisation of the 's' and 'd' states is suppressed above 100 K, and we should consider individual 's' and 'd' states.

The 's' state has by its definition a much larger value of v_F than the 'd' state; thus it contributes more to the electrical conductivity. The relaxation rate of the s state is determined by τ_{sd}^{-1} and τ_{ss}^{-1}, while the relaxation rate of the hybridised state is determined by τ_{dd}^{-1}, which is significantly larger because of the larger density of states of the 'd' state.

Therefore, the electrical conductivity after hybridisation is destroyed is dominated by $\tau_{ss}^{-1} + \tau_{sd}^{-1}$ and it decreases *more slowly* with temperature than at lower temperatures, where $\hbar/\tau_{dd} < J_{sd}$ and the conductivity is dominated by τ_{dd}^{-1}.

Two distinct cases exist.

(*a*) $\tau_{sd}^{-1} > \tau_{ss}^{-1}$. This is the situation in elemental transition metals. The density of states of the 'd' state is about a factor of 20 larger than that of the 's' state; therefore, even though the matrix element $V_{ss} = (\psi_s|\nabla V|\psi_s)$ is larger than the matrix element $V_{sd} = (\psi_s|\nabla V|\psi_d)$, the relaxation rate for s to d scattering dominates.

(*b*) $\tau_{ss}^{-1} > \tau_{sd}^{-1}$. In some transition-metal compounds the conduction-electron density of states is considerably higher than in the elemental transition metals. In binary intermetallic compounds like Nb_3Sn and UAl_2 the non-transition-metal atom contributes to the electronic density of states. The Sn and Al atoms possess s and p states, and the bands of these states are narrow since the non-transition-metal atoms are separated by the transition-metal atoms (Weger and Goldberg 1973). Moreover, the matrix element for scattering from a non-transition-metal s or p state to a transition-metal d state is small because of the small overlap of the wavefunctions. Thus, the non-transition-metal atoms in these compounds contribute to increase τ_{ss}^{-1} in comparison with τ_{sd}^{-1}.

Moreover, in the A15 materials the chain structure of the transition-metal atoms has a profound effect on the electronic states (Weger and Goldberg 1973, Weger 1978b). Chain atoms are much closer to each other than in elemental transition metals; in V_3Si the V–V distance along the chain is 2.36 Å, while in elemental vanadium the distance is 2.60 Å. Therefore the electronic density along the chains, midway between the atoms, is particularly large. A chain state $\psi = \exp(ikz)$ can be expanded as $\psi \approx 1 + ikz$, where the 1 signifies a state of s-type or σ-type symmetry, i.e. $3z^2 - r^2$, and z signifies a state of p_z-type symmetry. Thus for vanadium

$$\psi = \psi_{3d_\sigma} + ika\psi_{4p_z}$$

(and $4d_\sigma$ and $5p_z$ states for Nb) (figure 3). The density of p states at the Fermi level is (Mattheiss and Weber 1982) 21 electrons Ryd^{-1} per unit cell in V_3Si and 20 electrons Ryd^{-1} per unit cell in Nb_3Sn. This is approximately 15% of the total density of states. Together with the other s and p states, the total density of s and p states is approximately 20% of the total. This increases the value of τ_{ss}^{-1} by an order of magnitude. Moreover, the electronic density does not overlap that of the d_δ ($m = \pm 2$) states, whose band is very narrow, and thus they contribute significantly to the density of states at the Fermi level; thus the matrix element for s–d scattering is reduced and we have a situation where $\tau_{ss}^{-1} > \tau_{dd}^{-1}$.

The electronic density was measured by Staudenmann *et al* (1976, 1983) and the increased value along the chain, midway between the atoms, is striking. This can be described formally by using Wannier states on off-site positions (Mueller 1984). When these states are employed in a local Kohn–Appel (1971) formalism the contact approximation may be used. In this approximation, electron–phonon scattering terms in which the electrons do not change their site dominate. Thus τ_{sd}^{-1} is small. The contact approximation has been verified for Nb and V (Birnboim and Gutfreund 1976), but not yet for the off-site Wannier states. When $\tau_{ss}^{-1} > \tau_{sd}^{-1}$ the 's' and 'd' channels are completely decoupled.

In both cases (*a*) and (*b*), the resistivity at temperatures above the transition temperature increases linearly and the slope, using the Hopfield relation $\hbar/\tau = 2\pi\lambda k_B T$, indicates a value of λ that is smaller than that observed at lower temperatures but which

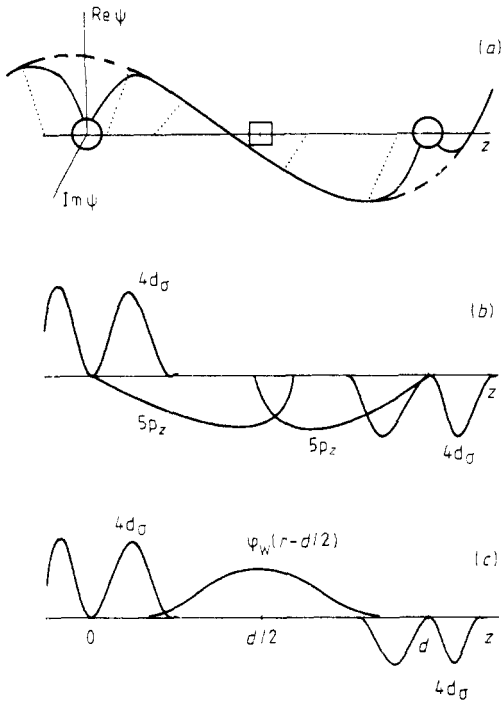

Figure 3. (*a*) A chain state is illustrated by a spiral in the space Re ψ–Im ψ–z. (*b*) Decomposition into spherical harmonics; the chain states contain a large amount of 5p state admixed into the 4d state. (*c*) Decomposition into Wannier states at off-site positions. There is a strong Γ_1 state on the chain midway between the atoms.

may still be appreciable (because of the large values of τ_{ss}^{-1} and τ_{sd}^{-1}). This agrees with experiment (figure 1).

In figure 2(*b*) we show a situation where both channels possess comparable values of the Fermi velocity and comparable contributions to the electronic density of states. Hybridisation gives rise to a very large, very sharp peak in the density of states near E_F. This sharp peak gives rise to a large value of λ at low temperatures, where $\hbar/\tau < J$, but at high temperatures, where $\hbar/\tau > J$, the two channels are again decoupled and the peak in the density of states disappears. Such a situation is known in some organic metals such as HMTSF–TCNQ, where the decoupling gives rise to a drastic change in the electronic density of states (Weger 1976, 1978a). A similar situation apparently exists in UAl_2 (Mueller *et al* 1984), and accounts for the knee in the ρ against T curve near 100 K.

In summary, the anomaly in the temperature dependence of ρ occurs when $\hbar/\tau \approx J$, and it requires (at least) two bands. Below this temperature the two bands are hybridised, and above it they are decoupled and the situation is very simple. This relation has nothing to do with $l \approx d$.

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